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Synthesis, Characterization and Biological Activity of Cis-Dioxomolybdenum(VI) Schiff base Complex $[MoO_2(L)_2]$

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Abstract

A new dioxo-molybdenum(VI) complex $[MoO_2(L)_2]$ was synthesized using 2,4-dihydroxy–benzalmethylene-o,o'-diethylphosphorohydrazonothionate (HL) as bidentate ON donor Schiff base ligand and $MoO_2(acac)_2$. This new compound was characterized by elemental analysis, IR, ^{1}HNMR, MS, UV/vis, and molar conductivity, and the six-coordinate structure with $[cis\text{-}MoO_2]^{2+}$ group in the complex was proposed on the basis of spectroscopic characterization. The insecticidal activity of the Mo(Ⅵ) complex to bollworm was investigated, and its effect on the cell survial rate of mung bean sprouts was also discussed. The results showed that the activities of the complex in killing aphid were more effective than that of methamidophos and lower in killing red spider than that of methamidophos. Moreover, the complex could promote the cell survial rate of mung bean sprouts.

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1. Introduction

Molybdenum plays a vital role in biological systems. Molybdenum complexe chemistry has gained much attention since molybdenum was found in the active sites of enzymes such as nitrogenase, aldehyde oxidase, xanthine oxidase, sulfite oxidase, nitrate reductase and xanthine dehydrogenase[1] . Moreover, for possessing one or more Mo=O unit in their active sites, these natural oxo-molybdenum enzymes are also widely used as catalysts in industrial processes such as olefin metathesis, olefin epoxidation etc [2]. To simulate the biological activities, a number of oxo-molybdenum complexes with stable and variable oxidation states varying from four to eight, have been investigated. In recent years, many studies focus on the syntheses of cis-$[MoO_2]^{2+}$ type complexes and their oxo transfer reactions, for example, epoxidation, sulfoxidation and phosphine oxidation reactions. However, it is still a challenge for people to understand well that the important properties of this metal and its interaction mechanism with living organism.

The hydrazone ligands have been applied in many fields, for instance, cancer drugs, schizophrenia, leprosy in pharmacy; plasticizers, polymer stabilizers, antioxidants, polymerization inhibitors in industry; herbicides, insecticides and plant stimulants in agriculture. Phosphorus(V) hydrazone has been reported as a precursor in the synthesis of Cu, Zn, Ni, Mn and Fe complexes [3], however, its molybdenum complexes have not yet been studied in detail. Herein, we report a new thiophosphorushydrazone (HL) derived from o,o'-diethylphosphorohydrazonothionate with 2,4-dihydroxybenzaldehyde and its corresponding dioxo-molybdenum(VI) complex. The biological activities of the complex including insecticidal activities to bollworm and promoting on the cell livability of mung bean seedlings have also been investigated.

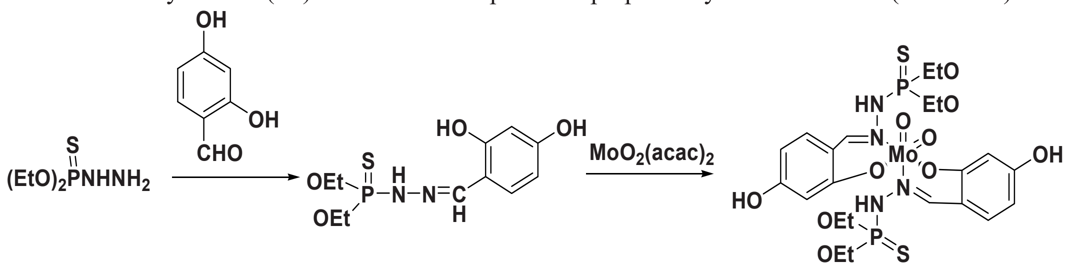
2. Experimental

2.1 Materials and Methods.

All materials were purchased from aldrich and used without further purification unless otherwise noted. The compounds o,o'-diethylphosphorohydrazonothionate and $[MoO_2(acac)_2]$ were synthesized according to the literature methods [3,4].

The schiff base ligand (HL) was prepared through the condensation of 2,4-dihydroxybenzaldehyde with o,o'-diethylphosphorohydrazonothionate.

The cis-dioxomolybdenum(VI) Schiff base complex was prepared by known method (Scheme 1)[4].



Scheme 1. The Synthesis Route of Complex

The synthesized ligand and its corresponding Mo(VI) complex were characterized by several spectroscopic techniques. 1H-NMR spectra were recorded on a Varian XL-200 spectrometer (d-DMSO). IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer using KBr wafers in the 200 – 4000 cm-1 range. Electronic spectra were recorded in DMF (N,N-dimethyllformamide) on a Shimadzu UV/Vis-265 spectrometer. C/H/N determination were performed by a Perkin-Elmer 240B spectrometer and MS spectra were obtained on an HP5988 Chromatography-Mass Spectrometry spectrometer. The content of Mo in complex was determined on a WFX-1F2 atomic absorption spectrophotometer. The electric conductivity of the compounds in DMF (1.0×10-4 mol•dm-3) at 298K were obtained on a DDS-IIA conductivity meter.

2.2 Activity test on killing bollworm

The leaves with ca. 2 mm in diameter were spread by different amounts of the as-prepared compound and eaten by bollworms for two weeks. The dead rate was counted after 24 hours later, and each test was repeated three time.

2.3 Impact of the complex on the cell livability of mung bean seedlings

Disinfectant mung bean seeds were soaked at 28 º C, and then sowed in nylon sieve to germinate. The leaves of the mung bean seedlings were cut into fragments with 1.5 cm in length after they grew to 6 cm.

Firstly, 5 mL compound with different concentration was added into the as-prepared leaves at room temperature, then the leaves were washed with distilled water after 4 hours soaking. Secondly, 5 mL 0.4% triphenyltetrazolium solution was used to soak leaf fragments after placed for 24 hours in dark, and then these fragments were washed with distilled water. Finally, the leaf fragments were immersed in 5 mL ethanol. The absorbance of the ethanol solution was determined under 530 nm in 721 spectrophotometer. The relative percentage of TTC(triphenyltetrazolium chloride) reduction was the relative cell livability.

2.4 Syntheses and characterization.

The schiff base (HL) was prepared by mixing o,o'-diethylphosphorohydrazonothionate (1 equiv) with 2,4-dihydroxy -benzaldehyde (1 equiv) in absolute EtOH (150 mL), then stirring for 1 h at room temperature. After removal of the solvent in vacuo, the product was a pale yellow oil (81.5% yield). Anal. Calcd for HL($C_{11}H_{17}N_2O_4PS$): C, 43.42;H, 5.59;N, 9.21%.Found: C, 43.69;H, 6.03;N, 9.27%. ^{1}H NMR (DMSO-d_6): δ = 1.4-1.6(m, 6H), 3.5（s, 1H）, 4.1-4.3(m，4H), 6.4-6.5（m, 3H）, 7.2-7.3（m，2H）, 8.1(s, 1H). M.S. m/z: 304, 150 , 125, 97 and 65.

The title dioxomolybdenum(VI) complex was prepared by mixing $MoO_2(acac)_2$ (acac= acetylacetonate) with the ligand (HL) in a 1:2 molar ratio using 30 mL absolute EtOH, followed by refluxing for 4 h. Reddish-brown powder were collected by filtration and dried in vacuo, The compound was recrystallized from absolute EtOH(40% yield). Anal. Calcd for [Mo $O_2(L)_2$] ($C_{22}H_{32}N_4O_{10}P_2S_2Mo$): C, 35.98; H, 4.39; N, 7.63, Mo13.06%. Found: C, 36.02; H, 5.03; N, 8.09, Mo14.00%.

3. Results and discussion

3.1 Synthesis and characterization.

The phosphorus hydrazide exhibits a remarkable hydrolytic stability. The dioxomolybdenum (VI) complex is relatively inert to oxygen and can exist in air or in solution for a long time. It is soluble in DMSO(dimethyl sulfoxide) and DMF, and it is non-electrolytes in DMF (Table 1).

The characteristic IR spectral data are summarized in Table1. The mononuclear complex exhibits two stretching frequencies [ν(O=Mo=O)] in the region 880–925 cm^{-1}, indicating the presence of cis-MoO_2 fragment. The greater shift of one of the oxo-molybdenum bands to lower frequency (880cm^{-1}) could be attributed to the intermolecular hydrogen bonding[5]. The blue-shift of IR band due to C=N is 6 cm^{-1} in the complex in comparison with the free schiff base. The value of 1626cm^{-1} shows the coordination of azomethine nitrogen to molybdenum center. Furthermore, two strong absorption bands appear at 420 and 630 cm^{-1}, assigned to the Mo-N and Mo-O stretching mode of vibration, respectively, which are absent in the free ligand. The result indicates that the schiff bases behave as bidentate ligand coordinating through phenolic oxygen and azomethine nitrogen[6].

Table1. Infrared, electronic spectral and molar conductance data of the compounds

Compound	λm	UV	IR(cm^{-1})				
	($S \cdot cm^2 \cdot mol^-$)	(nm)	N-H	C=N	Mo-N	Mo-O	Mo=O
HL	2.43	239，367	3208	1626			
$[MoO_2(L)_2]$	2.07	230，360	3260	1620	420	630	886，920

In the ^1H NMR spectra of HL can be assigned to only one set of the ligand resonances that the δ values are corresponding to identical protons in the HL ligand shift.

Table 2. Date and assignment of MS spectrum for HL

m/e	Relative Intensity	Fragment
304	54	$C_{11}H_{17}N_2O_4PS^+$
150	21	$C_7H_6N_2O_2^+$
125	34	$(CH_3CH_2O)(OH)PS^+$
97	100	$H_2O_2PS^+$
65	53	H_2SP^+

The electronic spectrum of the complex MoO_2L_2 displays two absorptions at 230 and 360 nm, corresponding to an intraligand π-π* transition and O(pπ)-Mo(dπ) charge transition band and the C= N n-π* transition,respectively. The phenomenon is also usually observed in cis-MoO_2 complex[7]. Compared with the shciff base, blue shift gives evidence of chelation of the schiff base through phenolic oxygen and azomethine nitrogen with the molybdenum center.

The mass spectrum for the schiff base (HL) has five prominent peaks and the molecular ion is observed at m/e 304, which is in agreement with the empirical formula $C_{11}H_{17}N_2O_4PS$ (Table 2).

The peak is observed at m/z 150, 125 and 65 belonging to the $C_7H_6N_2O_2^+$, $(CH_3CH_2O)(OH)PS^+$ and H_2SP^+ fragment, and the base peak at M/e 97 is corresponding to $(OH)_2PS^+$[8].

The compositions of the complex have been deduced based on the data obtained from elemental analysis, and the six-coordinate structure with $[cis\text{-}MoO_2]^{2+}$ group in the complex was proposed based on spectroscopic characterization.

3.2 Biological Activity

The activity of target complex is showed in Table 3 (c= 1×10^{-5} $mol \cdot dm^{-3}$) [9]. The data indicate that the complex bioactivity of killing aphid is higher than that of killing red spider. Meanwhile, the target compound is better than methamidophos in killing aphid, while it is worse than methamidophos in killing red spide.

Table 4 shows the influence on cell livability of mung bean seedlings.

Table 3. The death rate to kill bollworm of the complex and methamidophos (Ma)

Death rate(%) Bollworm / Compound	Aphid	Red spider
Methamidophos (Ma)	11.2	7.5
$MoO_2(L)_2$	13.9	4.7

Table 4. Influence on cell livability of mung bean seedlings.

Compound / C/ mol L^{-1}	1×10^{-2}	1×10^{-3}	1×10^{-4}	1×10^{-5}	1×10^{-6}
Methamidophos (Ma)	13.87	58.67	105.00	115.40	97.63
$MoO_2(L)_2$	80.00	99.0	143.00	115.00	104.00

It can be found that a higher concentration solution of the as-prepared compound can effectively inhibit cells livability (livability less than 100%), while a lower concentration below 1.0×10^{-3} mol/L can promote the growth of mung bean seedlings, and the concentration of 1.0×10^{-4}mol/L of compound exhibits the highest activity. Compared with methamidophos (Ma), the compound shows a higher cell livability of mung bean seedling. The date of table 4 shows a nonlinear relationship between the concentration of the compound and the cells livability of the mung bean seedlings.

4. Conclusions

A cis-dioxomolybdenum(VI) schiff base complex [$MoO_2(L)_2$] had been successfully synthesized and the six-coordinate structure containing [cis-MoO_2]$^{2+}$ group in the complex was proposed on the basis of spectroscopic result. The biological activity of cis-dioxomolybdenum(VI) schiff base complex [$MoO_2(L)_2$] showed that the complex was better than methamidophos in killing aphid, while worse than methamidophos in killing red spider. The complex can also promote the cell surival rate of mung bean sprouts. This paper will provide an insight into developing novel complexes with [cis-MoO_2]$^{2+}$ group.

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